1,059,599

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,059,599

Date of Application and filing Complete Specification: Dec. 4, 1963.

No. 47999/63.

Application made in United States of America (No. 242,224) on Dec. 4, 1962.

Complete Specification Published: Feb. 22, 1967.

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Index at acceptance:—H1 D(9C1X, 9C1Y, 9CY, 9D, 9Y, 21A, 21B, 51)

Int. Cl.:—H 01 j 39/36

COMPLETE SPECIFICATION

Separation of Ions which Differ in their Respective Specific Electric Charges

We, SIEMENS-SCHUCKERTWERKE AKTIENGESELLSCHAFT, a German Company, of Berlin and Erlangen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to the separation of ions which differ in their respective specific electric charges.

Patents nos. 773,689 and 904,033 disclose a method and apparatus for separating ions of different respective specific electric charges by shooting them into an electric high-frequency field between electrodes so that only ions of certain specific charges or mass can pass through the field to a collector electrode whereas other ions are caught by field-producing electrodes extending along the ion travel axis.

According to the principle of the above-mentioned known method of separation, the ions to be separated are shot into a periodically varying electric high-frequency field whose potential ø is a square function of the space coordinates x, y, z of the general form: —

$$ø = f(t)\cdot(\alpha x^2 + \beta y^2 - \gamma z^2) \qquad (1)$$

wherein f(t) denotes any desired periodic function of time (t), and α, β, γ, are positive constants which satisfy the equation $\alpha + \beta = \gamma$ but are otherwise selectable at will.

Used in practice is almost exclusively the special case $\gamma = O$, which requires that $\alpha = -\beta$. The following relates particularly to a field-electrode assembly satisfying the latter requirements. In such a field the travelling ions, under the influence of the high-frequency electric field, oscillate transversely of their forward travel in such a manner that the following two kinds of motions can be distinguished:

(1) The amplitudes of successive oscillations increase exponentially with time so that these ions impinge upon and are thus separated on the field-limiting electrodes at an earlier or later moment of their travel (unstable ions).

(2) The amplitudes of all oscillations do not exceed a given maximum value depending upon the particular starting conditions with which an ion commences its travel in the square-law potential field. If this maximum value of the oscillation amplitudes is within the space enclosed by the field-producing electrode assembly, the ions can pass through the entire spectrometer to reach a collector electrode or target at the end of the analyzing portion so that they can be observed by electrical measuring methods (stable ions).

Whether a travelling ion in the analyzer field is stable or unstable depends upon its specific electric charge e/m wherein *e* is the electric charge and *m* the mass of the particle. With suitably chosen field parameters these fields can thus be employed for separating ions of respectively different masses.

Heretofore, an analyzer field of the above-mentioned type has been produced with an assembly of four electrodes having, in the ideal case, hyperbolic surfaces facing each other, such an assembly of electrodes E being shown in Figure 1 of the accompanying drawings. For most purposes, however, such an arrangement of hyperbolic electrodes is sufficiently aproximated by four cylindrical rod electrodes of circular cross-section as shown at F in Figure 2 of the accompanying drawings. Even then the mutual adjustment of these electrode rods may turn out to be intricate because at the end of the field in the travel direction of the ions, denoted by an arrow Z in Figure 2, the spacing of each rod from the field axis, as well as the mutual distances of the rods, must be equal, and the entire system of rods should not possess any twist. The function f(t) can be given a desired

periodicity as well as a unidirectional and constant component by employing a high-frequency voltage and a superimposed direct voltage, for example with the aid of electric circuitry as described in the above-mentioned patent No. 904,033. In the method disclosed in that patent specification two voltages are supplied to the electrode system in symmetrical relation to ground potential. For this purpose, the direct voltage must possess respective equal positive and negative portions relative to ground, and the high-frequency voltage must be made accurately symmetrical, the latter being preferably done by employing a push-pull network, also as known from patent No. 904,033.

The amount of equipment and careful adjustment thus needed for successful and optimal performance of mass spectrometry according to the above-mentioned principle is considerable; and it is an object of this invention to afford the possibility of performing the desired mass-spectrometrical investigations with a smaller number of electrodes and correspondingly reduced requirements as to observance and maintenance of accurate adjustments.

According to one aspect of the invention there is provided a process for analyzing materials, in which ions which differ in their respective specific electric charges are separated by a method wherein the ions are directed substantially along an ion travel axis which is parallel to but spaced from the z-axis of a system (x, y, z) of space coordinates, the x- and y-axes of which system are perpendicular to the z-axis, and which passes through a region of electric field characterised by an electric potential ø which is substantially of the form

$$ø = f_1(t).(x^2 - y^2) + f_2(t),$$

$f_1(t)$ being a periodic function of time, and $f_2(t)$ being a periodic function of time or being constant in value, and wherein the said region is bounded by surfaces which restrict motion of the ions so that the coordinates of each of the ions between the two axial ends of the said region satisfy the condition $y \geqslant |x|$, whereby the ions travel through the said region on stable or unstable paths, depending upon their respective specific electric charges, so that the required separation is effected.

According to another aspect of the invention there is provided an apparatus for use in separating ions which differ in their respective specific electric charges, comprising first means for directing ions substantially along an ion travel axis which is parallel to but spaced from the z-axis of a system (x, y, z) of space coordinates, the x- and y-axes of which system are perpendicular to the z-axis and second means for producing in a region through which the ion travel axis passes an electric field characterised by an electric potential (ø) which is substantially of the form

$$ø = f_1(t).(x^2 - y^2) + f_2(t),$$

$f_1(t)$ being a periodic function of time, and $f_2(t)$ being a periodic function of time or being constant in value, the said region being bounded by surfaces which restrict motion of the ions, when the apparatus is in use, so that the coordinates of each of the ions between the two axial ends of the said region satisfy the condition $y \geqslant |x|$, whereby, when the apparatus is so used, the ions travel through the said region on stable or unstable paths, depending upon their respective specific electric charges, so that the required separation is effected.

The region of electric field may be produced between two elongate electrodes disposed on opposite sides of the ion travel axis, one of the electrodes being a fixed-potential electrode which is formed of two conductive and electrically interconnected planar surface members forming an angle with each other and extending in parallel and spaced relation to the ion travel axis between an ion source and a collector, and the other electrode consisting of a single rod and being located opposite the angled planar surface members in a position where the rod electrode bisects the angle and has a convex surface facing the axis. Between the fixed potential electrode and the rod electrode may be provided the electric circuit means required for applying the periodically variable electric potential for causing the differently charged ions to either pass from the source to the collector or to be caught by the field electrode (i.e. the rod electrode) depending upon whether the specific electric charge is such that the ions travel on stable or unstable paths.

For a better understanding of the invention, and to show how the same may be carried into effect, further reference will hereinafter be made, by way of example, to the accompanying drawings, in which:—

Figures 1 and 2 are diagrammatic perspective views of electrode assemblies in known apparatus for use in separating ions which differ in their respective specific electric charges.

Figure 3 is a diagrammatic perspective view of the electrode assembly of an embodiment of the new apparatus for use in separating such ions,

Figure 4 is an axial sectional view of the embodiment, Figure 5 is a schematic block diagram illustrating the operation of the embodiment,

Figure 6 is a circuit diagram of an excitation circuit for use with the embodiment,

Figures 7*a* and 7*b* are comparative diagrammatic transverse cross-sections of corresponding parts of a known apparatus and the

embodiment of the new apparatus respectively,

Figures 8, 9 and 10 are graphs, and

Figure 11 is an example of a mass-spectrogram obtained with the aid of the embodiment.

The field equation

$$\phi = f_1(t).(x^2 - y^2) + f_2(t) \qquad (2)$$

is analogous with the preceding field equation (1), but the principle of separation employed in the present invention is somewhat different from that previously employed and requires having the ion travel axis spaced from the origin of the x – y coordinate system.

The function $f_1(t)$ can be given a sinusoidal wave shape, although rectangular, saw tooth, or other periodic wave shapes are also applicable. The function $f_2(t)$ is preferably given a constant value for decelerating the ions or accelerating them as they enter into the analyser field. However, the function $f_2(t)$ may also be sinusoidal for speed modulation of the ions. An applicable excitation circuit for superimposing a high-frequency voltage and a unidirectional voltage according to function $f_1(t)$ is given in Figure 6.

With reference to Figure 3, the assembly comprises a field electrode 1, in the form of a cylindrical rod, and a reference electrode having two planar portions 2 and 3. The field electrode 1 is parallel to the reference electrode and at equal distances from the two planar portions 2, 3, so that a plane including the line along which the two portions meet and bisecting the angle between the two portions would include also the axis of the cylindrical field electrode 1. Each of the planar portions has a width greater than the diameter of the field electrode.

The two planar portions of the reference electrode make up a single angular structure (2, 3) and are made of sheet metal, wire-mesh material, arrays of wires, or the like. The angle formed by the two portions 2 and 3 is 90°, so that the respective surfaces represent the coordinate planes $y = +x$ and $y = -x$ of a single quadrant. However, other angles between 60 and 120° are applicable, as well as smaller and larger angular values (being substantially greater than 0° and substantially less than 180°, however), depending upon the desired degree, yield or accuracy of separation. Where such other angle is used, of course, it is equal to the angle between x- and y-axes of the coordinate system concerned.

If the two planar portions of the reference electrode are formed as a single sheet-metal structure, this structure may simultaneously constitute a vacuum wall portion of a vacuum vessel within which the separation of the ions is to be effected.

During operation the angular reference electrode is kept at ground potential, whereas a field potential comprising a high-frequency voltage $V \cdot \cos \omega t$ and a superimposed negative direct voltage $-U$ is impressed upon the field electrode, this being schematically indicated in Figure 3.

Since such an electrode arrangement is not symmetrical about the z-axis, compared with the symmetry about the four-pole axis Z in the known equipment as represented in Figure 2 no ion trajectories are possible with the arrangement of Figure 3 that constitute oscillations about such a symmetry axis. Nevertheless, ions can pass through the periodic field produced between the electrodes of Figure 3, because the choice of suitable field parameters affords the production of ion paths which for many oscillations fully extend alongside, without actually crossing, the four-pole axis. Thus, the arrangement of Figure 3 can be used to separate ions that oscillate alongside the four-pole axis from ions that tend to oscillate about that axis. Added to this novel effect is the separation effect caused by the different increases in amplitude of ion oscillations mentioned above.

The apparatus illustrated in Figure 4 comprises an evacuable vessel 4 of elongate and substantially cylindrical shape in which the field electrode 1 (as in Figure 3) is mounted so as to be located in bisecting relation to the angle formed by the two planar portions of the reference electrode (as in Figure 3) here denoted by 2. The field electrode 1, which may either be solid or hollow, is insulated from the angular reference electrode 2 which in turn is mounted on the wall of the vessel 4 by means of holders 5. These holders may consist of metal thus placing the reference electrode 2 on ground potential since the vessel 4 also consists of metal and is grounded.

The central analyser portion of the vessel has a lateral branch nipple 6 for connection to a vacuum pump and is provided with end flanges 7 and 8 for connection to respective closure portions 9 and 10 on which an ion source 11 and a collector electrode 12 respectively are mounted. In operation a beam of ions is issued from the source 11 and is directed, with the aid of an effective aperture through which the ions must pass and which is defined between the lower edge of a diaphragm 12′ and the apical portions of the electrode 2, substantially along an ion travel axis which extends between and parallel to the two electrodes producing the electric analyser field. A corresponding aperture-defining diaphragm 13 is mounted in front of the collector 12. A neck portion 14 of the analyser vessel 4 carries an insulated conductor 15 in contact with the field electrode 1.

Referring to Figure 5, which indicates only the electrical components of the analysing components, proper, the ion source 11 is connected to a current-supply unit 21 which is preferably energized from a mains supply line. The ion accelerating voltage, for example

92 volts, is then connected between the ions source and the angle structure of the reference electrode 2. The ions themselves are produced by electron collision in the source 11. For this purpose the electrons are emitted from an incandescent filament K and shot into the source 11. Lenses L serve to focus the ions into the analyser field, the mean path of the ions when entering the field being along the ion travel axis. The field electrode 1 is connected through its lead 15 and a capacitor 22 to a high-frequency generator 23 and also through an inductance coil 24 to a direct-voltage source 25 which may consist of a rectifier. The high-frequency generator and the direct-voltage source 25 are preferably energized from the above-mentioned utility power-supply line to which the unit 21 is connected. The collector electrode 12 is grounded through the input stage of an amplifier 26 whose output circuit is connected to a recording instrument 27.

An example of a circuit, including the high-frequency source 23 and the rectifier 25, for applying field voltage to the field electrode 1 is more fully shown in Figure 6.

The single cylindrical rod field electrode 1 is held in correct position with respect to the rectangular reference electrode 2 by means of four insulating holders of the same height. Two of these holders are shown at 17 and 18 in Figure 4. They are cemented to one of the planar surfaces of the reference electrode structure 2 and extend in perpendicular relation thereto, the other end of each holder being cemented to the field electrode rod 1. The two other insulating holders, not visible in Figure 4 are arranged in the same manner except that they are fastened to the other planar surface of the reference electrode structure 2. The number of possible adjusting errors is thus considerably reduced, compared with the known four-pole system.

The apparatus of Figure 4 can be given a smaller over-all size than a four-pole apparatus of the known type. A suitable basis of comparison is a given ion current at the collector. In comparison with a four-pole spectrometer of the known type with four cylindrical rods of unit diameter, a corresponding spectrometer according to Figure 4 with the same unit diameter of the single rod electrode has only one-half of the ion current. This is due to more unfavourable conditions with respect to the shooting of ions into the analyser field. Since the utilizable ion current increases approximately in linear proportion to the cross-sectional surface of the analyser field, a spectrometer according to Figure 4 can be made rated for the same ion current as a four-pole spectrometer of the known type with rods of unit diameter, if the rod diameter of the single field electrode is increased to the value $1 \times \sqrt{2}$. It follows that in this case a spectrometer according to Figure 4 can be considerably smaller than an apparatus of the known type. This is exemplified by the comparison presented by Figure 7*a* and 7*b*, the former showing the geometric relations of a four-pole apparatus and the latter the corresponding relations of an apparatus according to Figure 4. The increase in rod diameter and the elimination of three rod electrodes just compensate each other with respect to their influence upon the necessary high-frequency power. The ratio of the demand for high-frequency power to the separated ion current, therefore, is substantially the same for both apparatuses.

If desired, embodiments of the invention also afford a possibility of a considerable simplification of the electrical circuitry required for operating the separator. It is no longer necessary to generate two alternating voltages 180° phase-displaced from each other, but suffices to provide for only one alternating voltage. The necessity of push-pull circuitry is also eliminated, and only one superimposed direct voltage (negative relative to ground potential) is required, this being apparent by the example of circuitry illustrated in Figure 6. It will be understood, of course, that modified circuits are applicable if this is desirable for special purposes.

The paths of ions that reach the collector in the apparatus according to Figure 4 are such that a quasi-optical image of the entrance aperture or diaphragm gap is projected upon the exit diaphragm 13. By virtue of this property, the mass separating apparatus according to Figure 4 achieves a given resolving power with approximately one-half of the ion-travel time required by an otherwise comparable four-pole mass spectrometer. This affords a higher ion current, a higher resolving power, or a shorter structural length of the apparatus, as may be desired in a particular case, in comparison with the four-pole apparatus.

In operation the field potential in the space between the cylindrical rod field electrode and the angle structure of the reference electrode can be defined by the equation:

$$\phi = f_1(t) \cdot \sum_{1}^{\infty} a_n \left(\frac{d}{D} \right)^n \cos(n\varphi + \epsilon_n)$$

and is realized only for the condition

$$-\frac{\pi}{4} < \varphi < \frac{\pi}{4}.$$

In the foregoing equation as well as in the following derivations, the meaning of the terms employed is as follows:

ϕ = potential

f_1 = potential of the field electrode with respect to the rectangular reference electrode,

f_2 = additional potential of both electrodes with respect to ground,
t = time,
t_o = moment at which the ion enters into the analyser field,
a,q = substitutions in Mathieus' differential equation,
d,φ = coordinates of a polar coordinate system (see Figure 8),
D = distance of the field electrode rod from the apex of the angle,
x,y,z = coordinates of a rectangular coordinate system (see Figure 8),
ϵ = phase constant,
n,s = summation indices,
ξ = variable of Mathieus' differential equation,
U = direct voltage,
V = high-frequency amplitude,
ω = circular frequency,
β = parameter of Mathieus' differential equation,
m = ion mass,
e = elementary charge,

Figure 8 shows a cross-section of the two electrodes in diagrammatic form for the purpose of indicating some of the above-mentioned magnitudes required for the computation presented below.

Figure 9 is a graph showing on the abscissa the parameter magnitudes *q* and on the ordinate the corresponding parameter magnitudes *a*. A stable range of the ions, depending upon the parameters *a* and *q* is indicated by hatching.

Figure 10 shows schematically the path of a particle in the system *y* relative to *t* or *z*. The important property of this beat-frequency path is the fact that the ion travel extends for a relatively long period of time alongside the t-axis or z-axis.

The analytic treatment of the equation for the motion of the ions in the field between the field electrode 1 and the reference electrode 2 becomes particularly simple if the coefficient a_2 is greatly preponderant to all others. This occurs, for example, when the diameter D_{st} of the field electrode is equal to 2.3 times the field diameter D (as will more fully appear from Figure 8 described below). The first approximation for the potential ø, neglecting all values of a_n ($n \neq 2$), and taking $\epsilon_n = 0$, can then be written as

$$\phi = f_1(t) \cdot a_2 \cdot \left(\frac{d}{D}\right)^2 \cdot \cos 2\varphi$$

After applying rectangular (Cartesian) coordinates:

$$\left.\begin{aligned} x &= -d \cdot \sin\varphi \\ y &= d \cdot \cos\varphi \end{aligned}\right\} \text{ for } (y \geqslant |x|)$$

and inserting the potential

$$f_1(t) = -(V \cdot \cos \omega t + U)$$

the equations for the motion of the ions, using the substitutions

$$a_2 = 1;\ \omega t = 2\xi;\ a = \frac{8eU}{m\omega^2 D^2};\ q = \frac{4eV}{m\omega^2 D^2}$$

lead to Mathieus' differential equations

$$\ddot{x} + (a + 2q \cdot \cos 2\xi)x = 0$$
$$\ddot{y} - (a + 2q \cdot \cos 2\xi)y = 0.$$

The solutions of these differential equations result in the ion paths in the spectrometer. The constitute, in the $x-z$ plane as well as in the $y-z$ plane, complicated oscillations which are generally so constituted that the ions impinge upon one of the two electrodes during the first oscillation and are thus eliminated. Consequently, in order to have an ion path extend through the entire analyser field, the folowing three conditions must be met:

(a) there must always be $y > 0$
(b) there must always be $y > |x|$
(c) there should always be $y < D$.

Now, there is indeed a combination of parameters *a* and *q* which permits satisfying all of these three conditions simultaneously. If the ions are shot into the analyser field substantially in parallel relation to the z-axis, then within the range indicated in the graph of Figure 9 by hatching, the motion of the ion in the y-direction can be described in approximation by the following equation:

$$y(t_o + t) = 2.38 \cdot y(t_o) \cdot \frac{1}{\beta} \cdot \sin\frac{\beta}{2}\omega t \cdot \sum_{s=1}^{\infty}(a_s \cdot s \cdot \sin s\,\omega t_o) \cdot \left\{1 + \sum_{1}^{\infty} a_s \cdot \cos[s \cdot \omega(to + t)]\right\},$$

wherein
$y(t_o)$ denotes the starting value of the ion motion at the moment t_o,
a_s denotes the development coefficient, and
$\beta = k^2$, wherein k is a measure for the distance of the (a, q)-value from the left-hand stability limit (of the hatched area shown in Figure 9).

Independently of the phase ωt_o of the high-frequency voltage with which the ion commences its motion in the analyser field, the travel path is a beat-frequency oscillation on account of the terms $\sin \frac{\beta}{2} \omega t$ and $0 < \beta < 1$, this being schematically represented in the graph of Figure 10. Because a_1 is smaller than unity, the outstanding property of this beat oscillation upon which the entire method is predicated, is the fact that the ion trajectories extend for a prolonged interval of time alongside the t-axis or z-axis, thus satisfying the above-mentioned condition (a). The length of the beat oscillation, measured in the number of high-frequency periods, depends only upon the (a, q)-value of the ion and, theoretically, can be made as long as desired. However, since the spacial length depends upon the speed of the ions, it is possible to adapt the spacial length of the beat oscillation by variation of the ion speed to an optimal extent to the length of the spectrometer equipment. In order to ascertain an ion at the collector, the first node of its beat oscillation must be located behind the end of the analyser field. Consequently all of the ions whose energy is below a given minimum value are separated on the angular reference electrode. This minimum energy is proportional to dq, this being the distance of the (a, q)-value from the left stability limit (Figure 9). When the (a, q)-value migrates toward the right in the stability diagram, then the beat oscillations become successively shorter and with a given ion energy a point is ultimately reached in which all ions are separated upon the angular reference electrode. Consequently a mass separation is possible along the entire y-stability limit, the ion currents being to a great extent independent of the adjusted ratio a/q. This constitutes a considerable advantage over the known mass filters where the constancy of this ratio has a considerable influence upon the measured intensity ratio.

The condition (b), namely $(y > |x|)$, can be satisfied by suitable ion injection conditions y_o. Besides, if an ion does not meet this requirement, it is automatically eliminated in the analyser field.

The condition (c) determines the position of the working range in the stability diagram near the y-stability limit. The width of this range is given by the condition (a).

The spectrogram shown in Figure 11 is an example of those taken with apparatus as described above with reference to Figures 3 to 6. The horizontal axis of the diagram indicates mass numbers, the vertical amplitudes are indicative of the ion current flowing to the collector as represented by the deflection of the recording instrument. The spectrogram was taken for the range of masses 14 to 45. The apparatus used had an analyser field length of 27 cm, a field diameter of 1.5 cm. The frequency of field excitation applied for separation of mass 28 was 1.54 megacycles per second. $f_2(t)$ was always $\equiv 0$, which means that the reference electrode was on ground potential. The total pressure of nitrogen-containing gas supplied to the interior of the apparatus was 10.3×10^{-7} mm. Hg. The measuring range for masses 14 to 18 was found to be $3 \cdot 10^{-10}$ Amperes (as represented by the full deflection of the measuring or recording instrument). The corresponding measuring range for masses 19 to 45 was $1 \cdot 10^{-10}$ A.

The sensitivity (calibrated with N_2) was 3.0×10^{-4} A/mm.Hg. For taking the illustrated diagram an ion accelerating voltage of 92 V was applied between the ion source box 11 and the reference electrode 2. The electron emission from the ion source was 1.2 mA. The entrance diaphragm (12 in Figure 4) as used had a diaphragm aperture of 2 mm². The resolving power was approximately 190 and the dwell time of the ions in the analyser field was 16.5 high-frequency periods.

The diagram shows that the gas contained ions predominantly of masses 18 and 28 but also noticeable quantities of mass 44. A particular value of the diagram, as well as many others taken for other gases or under other operating conditions, resides in the fact that it combines a good shape of the spectral lines or peaks with relatvely high sensitivity.

WHAT WE CLAIM IS:—

1. A process for analysing materials, in which ions which differ in their respective specific electric charges are separated by a method wherein the ions are directed substantially along an ion travel axis which is parallel to but spaced from the z-axis of a system (x, y, z) of space coordinates, the x- and y-axes of which system are perpendicular to the z-axis, and which passes through a region of electric field characterised by an electric potential (ø) which is substantially of the form

$$ø = f_1(t).(x^2 - y^2) + f_2(t),$$

$f_1(t)$ being a periodic function of time, and $f_2(t)$ being a periodic function of time or being constant in value, and wherein the said region is bounded by surfaces which restrict motion of the ions so that the coordinates of each of the ions between the two axial ends of the said region satisfy the condition $y \geqslant |x|$, whereby the ions travel through the said region on stable or unstable paths, depending upon their respective specific electric charges, so that the required separation is effected.

2. A process as claimed in claim 1, wherein the ions are supplied by an ion source disposed at one end of an evacuated vessel, the ion travel axis extends within the vessel from the ion source to a collector disposed at the oppo-

site end of the vessel, and the electric field is produced between two elongate electrodes which are disposed on opposite sides of the ion travel axis, the longitudinal axes of the electrodes being parallel to the ion travel axis, and that part of the profile of the cross-section of each electrode which corresponds to one of the opposed respective surfaces of the electrodes being uniform over the length of the electrode, whereby only ions which travel on stable paths reach the collector.

3. A process as claimed in claim 2, wherein the electric field is produced by the application to one of the electrodes with respect to the other of a high-frequency voltage superimposed on a direct voltage.

4. A process as claimed in claim 2 or 3, wherein one of the two electrodes is a field electrode the surface of which facing the ion travel axis is convex, and the other of the two electrodes is a reference electrode having a planar surface portion facing and parallel to the ion travel axis which planar surface portion extends the length of the reference electrode.

5. A process as claimed in claim 4, wherein the said planar surface portion has a width, perpendicular to the z-direction which is greater than that of the field electrode.

6. A process as claimed in claim 4 or 5, wherein the reference electrode has two such planar surface portions, at an angle between 60 and 120° with one another and disposed so that a plane bisecting the said angle would include the ion travel axis and bisect the said convex surface of the field electrode.

7. A process as claimed in claim 6, wherein the said angle is a right angle.

8. A process as claimed in claim 6 or 7, wherein the two planar surface portions meet in a line which is parallel to and spaced from the ion travel axis.

9. A process as claimed in any one of claims 4 to 8, wherein the field electrode is cylindrical.

10. A process as claimed in any one of claims 4 to 9, wherein the reference electrode is made of metal.

11. A process as claimed in any one of claims 4 to 10 when they are read as appendant to claim 3, wherein the reference electrode is earthed, and the high-frequency voltage superimposed on the direct voltage is applied to the field electrode.

12. A process as claimed in any one of claims 2 to 11, wherein the electrodes are disposed within a central analyser portion of the vessel, and the ion travel axis is defined by two apertures, one of the apertures being defined by means of a first diaphragm which is disposed between the ion source and the analyser portion, and the other aperture being defined by means of a second diaphragm which is disposed between the analyser portion and the collector.

13. A process for analysing materials, in which ions which differ in their respective specific electric charges are separated by a method substantially in accordance with any embodiment hereinbefore described with reference to the accompanying drawings.

14. An apparatus for use in separating ions which differ in their respective specific electric charges, comprising first means for directing ions substantially along an ion travel axis which is parallel to but spaced from the z-axis of a system (x,y,z) of space coordinates, the x- and y-axes of which system are perpendicular to the z-axis, and second means for producing in a region through which the ion travel axis passes an electric field characterised by an electric potential (ϕ) which is substantially of the form

$$\phi = f_1(t).(x^2 - y^2) + f_2(t),$$

$f_1(t)$ being a periodic function of time, and $f_2(t)$ being a periodic function of time or being constant in value, the said region being bounded by surfaces which restrict motion of the ions, when the apparatus is in use, so that the coordinates of each of the ions between the two axial ends of the said region satisfy the condition $y \geqslant |x|$, whereby when the apparatus is so used, the ions travel through the said region on stable or unstable paths, depending upon their respective specific electric charges, so that the required separation is effected.

15. An apparatus as claimed in claim 14, wherein the said first means comprises an ion source disposed at one end of an evacuable vessel and a collector disposed at the opposite end of the vessel, the arrangement being such that the ion travel axis extends within the vessel from the ion source to the collector, and wherein the said second means comprises two elongate electrodes disposed on opposite sides of the ion travel axis with their longitudinal axes parallel to the ion travel axis, that part of the profile of the cross-section of each electrode which corresponds to one of the opposed respective surfaces of the electrodes being uniform over the length of the electrode, the arrangement being such that when so used only ions which travel on stable paths reach the collector.

16. An apparatus as claimed in claim 15, wherein the said second means further comprises electric circuit means for applying to one of the electrodes with respect to the other a high-frequency voltage superimposed on a direct voltage.

17. An apparatus as claimed in claim 15 or 16, wherein one of the two electrodes is a field electrode the surface of which facing the ion travel axis is convex, and the other of the two electrodes is a reference electrode having a planar surface portion facing and parallel to the ion travel axis, which planar surface

portion extends the length of the reference electrode.

18. An apparatus as claimed in claim 17, wherein the said planar surface portion has a width, perpendicular to the z-direction, which is greater than that of the field electrode.

19. An apparatus as claimed in claim 17 or 18, wherein the reference electrode has two such planar surface portions, at an angle between 60° and 120° with one another and disposed so that a plane bisecting the said angle would include the ion travel axis and bisect the said convex surface of the field electrode.

20. An apparatus as claimed in claim 19, wherein the said angle is a right angle.

21. An apparatus as claimed in claim 19 or 20, wherein the two planar surface portions meet in a line which is parallel to and spaced from the ion travel axis.

22. An apparatus as claimed in any one of claims 17 to 21, wherein the field electrode is cylindrical.

23. An apparatus as claimed in any one of claims 17 to 22, wherein the reference electrode is made of metal.

24. An apparatus as claimed in any one of claims 17 to 23, wherein the reference electrode is earthed, and the high-frequency voltage superimposed on the direct voltage is applied to the field electrode.

25. An apparatus as claimed in any one of claims 15 to 24, wherein the electrodes are disposed within a central analyser portion of the vessel, and the ion travel axis is defined by two apertures, one of the apertures being defined by means of a first diaphragm which is disposed between the ion source and the analyser portion, and the other aperture being defined by means of a second diaphragm which is disposed between the analyser portion and the collector.

26. An apparatus for use in separating ions which differ in their respective specific electric charges, substantially in accordance with any embodiment hereinbefore described with reference to Figures 3 to 8 of the accompanying drawings.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1967. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

1059599 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG.1

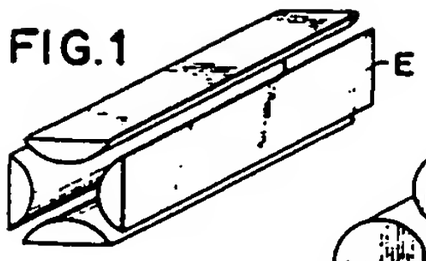
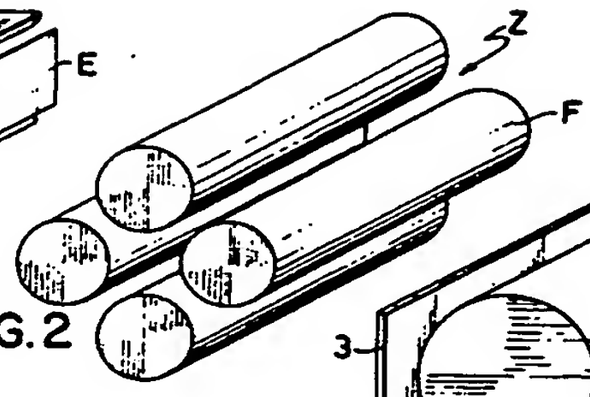


FIG.2



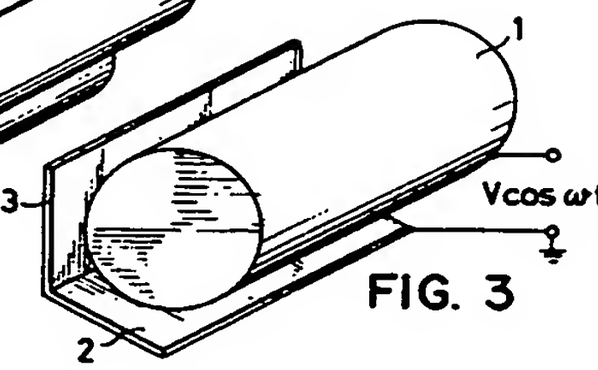


FIG. 3

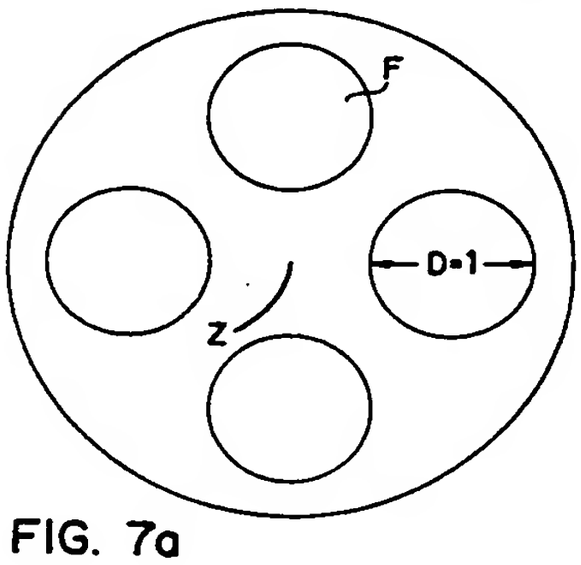


FIG. 7a

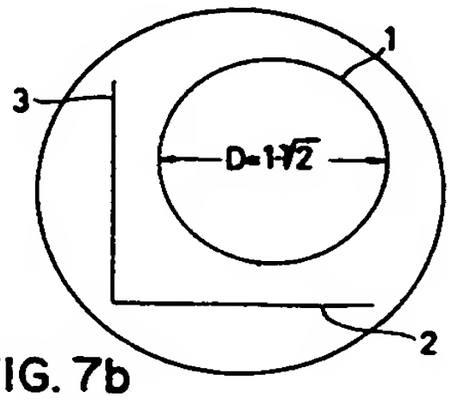
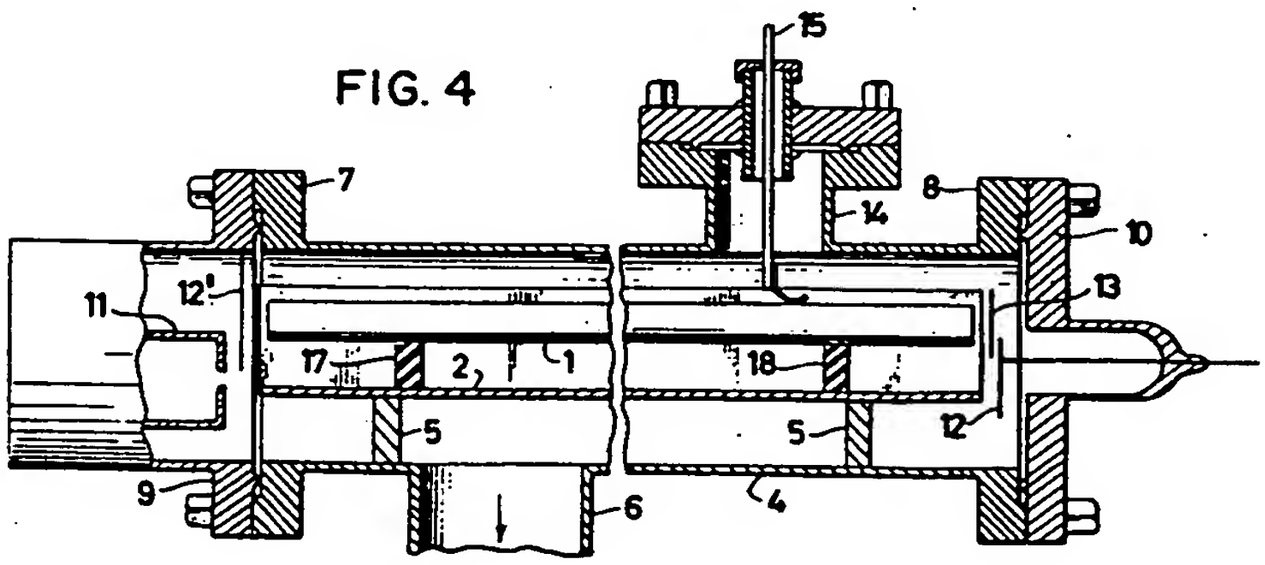


FIG. 7b

FIG. 4



1059599 COMPLETE SPECIFICATION
3 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheets 2 & 3

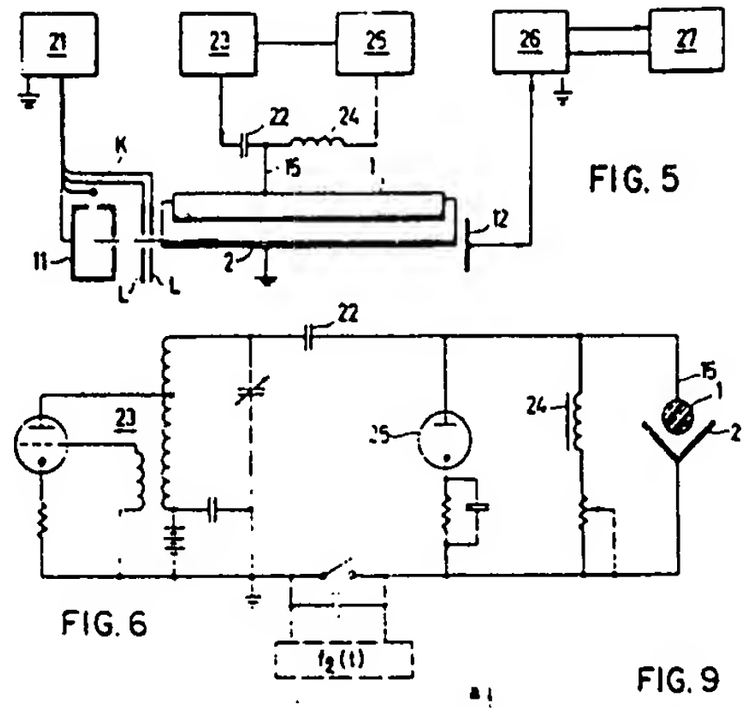


FIG. 5

FIG. 6

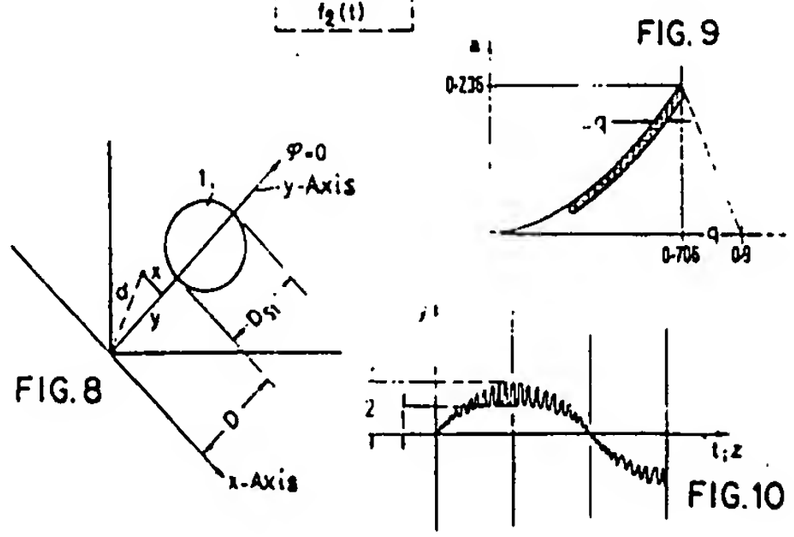


FIG. 9

FIG. 8

FIG. 10

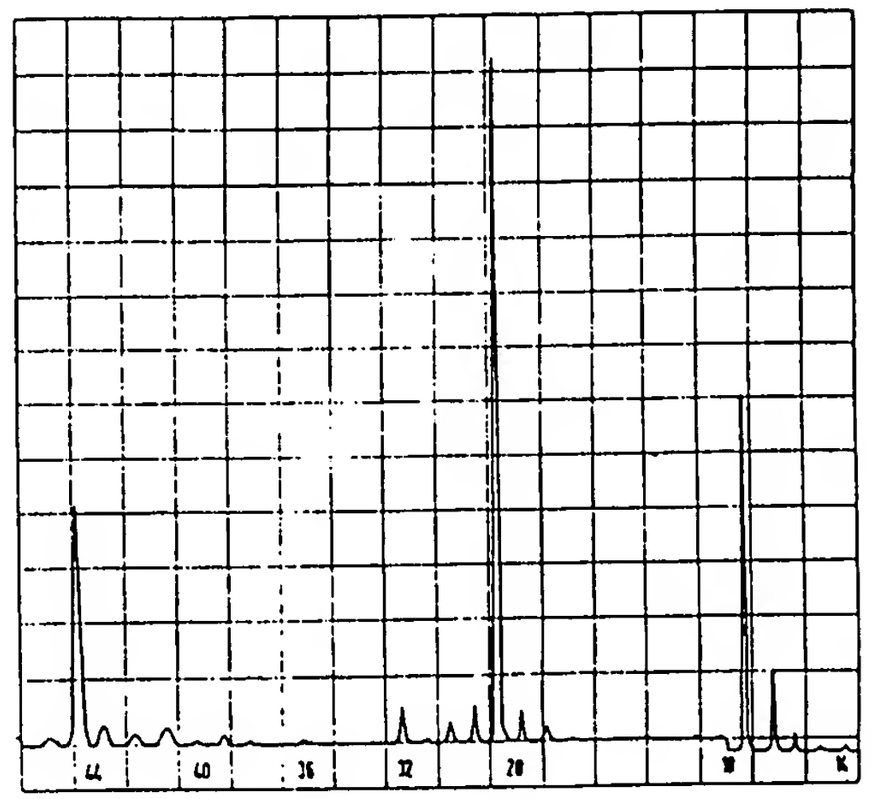


FIG. 11